Study of The Structural, Morphological and Electrical properties of WO₃ Nano Powders Which Use as Gas Sensors

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ABSTRACT: Nano-powders of tungsten oxide (WO₃) have been prepared by high energy ball-milling for various spans of mill time (1-18 h). The crystal structure, surface morphology of the prepared WO₃ nano powder were characterized by X-ray diffraction and scanning electron microscope. Thick films of WO₃ Nano-powders were prepared by printing painting chemical method to use them as gas sensors for methanol vapor at different operating temperatures, Their I-V characteristics were studied by using devices KEITHLEY 237. The effect of the milling time on the crystal structure, surface morphology, and electrical properties are reported.

1. INTRODUCTION

In the current materials science research, great emphasis has been placed on the nano materials in order to study the unique physical properties.

The surface-to-bulk ratio for the nano materials is much greater than that for coarse materials, in nano materials, a large fraction of the atoms is present at the surface, and hence, the surface properties become paramount. Another important factor associated with the depth of charge region and the surface space is affected by the relation between gas adsorption and the particle size. These features of nano particles make the materials particularly good for their applications as gas sensors [1].

Tungsten oxide-based gas sensors are efficient for detecting reducing gases such as hydrogen, carbon monoxide, ammonia gas etc. These devices are also capable to detecting many other compounds in vapor state such as ethanol, methanol, propanol, etc. within the atmosphere [2,3]. Thus, in order to be able to use these devices for detecting various pollutants in the atmosphere, it is necessary to understand their behavior when placed in contact with tungsten oxide-based gas sensors [4]. The ability to detect organic compounds vapors is very important since these compounds are widely used in industrial application and sometimes as chemical warfare gases.

Methanol is a hydrocarbon compound, miscible with water, has the chemical formula CH₃OH, it is considered one of the pollutants of the environment, It dissolves easily in water and soil with high concentrations, When methanol is left to evaporate in the air, it will form formic aldehyde and formic acid, which also contribute in air pollution, and damage to living organisms especially human because it destroys many cells of the body, especially the retina.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of WO₃ Nano-powders

WO₃ nano powders were prepared by high energy ball milling (HEBM) method. WO₃ powders were milled by (Activator 2S, Russia) system during time from 1 to 18 h with step at 3 h. The milling conditions and the material compositions are summarized in Table.1

Table 1. Milling conditions in the high energy ball mill.

Raw materials	Materials of jars & balls	Ball to powder weight ratio	Volumes of jars	Ball diameters	Jar speed	Disc speed
WO ₃	WC	1:20	80[ml]	10[mm]	320 [rpm]	640[rpm]

2.2. Preparation of thick films:

We used painting chemical method to prepare thick films which we can explain it as follow:

The WO_3 nano powder was mixed with distilled water to make paste, which was painted on the glass substrates soda-lime with dimensions $10\text{mm} \times 20\text{mm}$ patterned by silver-copper electrodes, then the thick films were left at 300 K for 6-12 h in air atmosphere

3. RESULTS AND DISSECTION

3.1. Structural properties for prepared nano powders:

The X-ray diffraction patterns of WO_3 nano powders were carried out using a STOE transmission Stadi-P diffractometer with monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The wavelength was selected using an incident-beam curved-crystal germanium $\text{Ge}(111)$ monochromator with a linear position-sensitive detector (PSD). The patterns were scanned over the angular range $20\text{--}50^\circ(2\theta)$ with a step length of the PSD of $0.5^\circ(2\theta)$ and a counting time of 30s per step.

The X-ray diffraction patterns for WO_3 raw material and milled powders are shown in Figure 1. The X-ray patterns indicate that WO_3 crystallize in Triclinic crystal structure with space group (P-1) and cell parameters ($a = 7.3126 \text{ \AA}$, $b = 7.5252 \text{ \AA}$ and $c = 7.689 \text{ \AA}$), angles between each pair of unit cell axes ($\alpha = 88.85^\circ$, $\beta = 90.91^\circ$, $\gamma = 90.94^\circ$) [5,6].

Figure 1. X- ray diffraction patterns at selected milling times for the WO_3 sample milled at 320/640 rpm in comparison with raw material of WO_3

X-ray pattern of WO_3 powder oxide before milling shows high intensity of Bragg peaks due to the micro powder oxide, with advance milling X-ray patterns show a gradual broadening and simultaneous decreasing in intensity; while that the position of the peaks have no changes and no new peaks appear just only low peaks disappearance which mean that the crystal structure of WO_3 powder oxide doesn't change during the milling but the average of crystal size of WO_3 powder is changing considerably.

The average of the crystal size was evaluated based on diffraction peaks of (200), (020) and (002) by using measurement program fit ,and their mean values were adopted as an average crystal size (diameter D).

Figure 2. Size of WO_3 nano crystal of ball-milled composites versus milling time.

Figure 2 shows the rapid decreasing of the average of the crystal size for WO_3 powders to nano powders (from about 113 nm in raw material to about 25 nm after 3h milling) then become stable about (17nm) from (9-15h) We can say that the milling with HEBM produces nano crystallite This is done to obtain large numbers of nano dislocations and accompanying a stress fields, where the crystal lattice constants are changing then the periodic length in crystal lattice is reduced and the crystal size decreased. This is agree with the broadening and the decreasing of intensity of X-ray diffraction peaks taken after milling to a specific time, and agree with the scientific papers [4,7]. So we can explain cause of stable the curve from (9-15h) the crystallites begin absorb stresses and pressures and this time that electrical forces between particles equal their weight forces.

3.2. Morphological properties for nano powders:

Scanning electron microscope SEM (TESCAN VIGA II XMU) was used for surface morphology study, figure 3 shows the SEM images of the nano powders of WO_3 milled at different times:

Figure 3. SEM images of WO_3 powders during various periods milling: (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, (f) 15 h, (g) 18 h.

As we see the powders consist of WO_3 particles of various sizes ranging from about 216 nm to 72 nm tended to increase (about 75 nm) with increasing milling time. Considering the particle sizes shown in Figure 3 and the crystallite sizes calculated from X-ray patterns (Figure 2), most of the particles are agglomerates consisting of two or more crystallites.

Figure 4 shown the average particle size that taken by SEM as a function for milling time

Figure 4. Size of WO_3 nano particles of ball-milled composites versus milling time

We note from the figure 4 a gradual decreasing of the particle size with increasing milling time until 15 h then as increasing milling time as particle size, which is explained as: at the beginning of milling, particles respond, and disintegrate into softer particles, coupled with electrically charged surfaces are opposite because of direct cracking for these particles which exposure to stresses and pressures and the forces of cut affecting on areas of weakness in the granular structure, when arrived at specific nano scale dimensions the electrical forces between the nano particles become greater than the forces of their weights, because of the ability materials to conformation these particles are clustered together and formed larger than the previous one so we see it by SEM like particle one [8].

3.3. Electrical properties for thick films:

The conductivity measurements are carried out in a pressure-controlled chamber during heating the thick films in a gas flow apparatus equipped with an external controlled heating facility. The resistances of the thick films are measured by the two-probes method with silver-copper electrode deposited on the films by chemical painting method. The nature of the contact is verified

to be ohmic by I-V Characteristics. A thermocouple was attached to the thick films holders for monitoring and controlling the operation during conductance measurements. The resistance of the sensors in the presence of either pure air (R_{air}) or the different pollutants (R_{gas}) at different concentrations is monitored and stored in a PC. All films prepared from powdered metal oxides used underwent for the same conditions and the measurement of electrical parameters applied to the device KEITHLEY 237 using the following parameters which shown in the table (2) [9].

Table 2. Parameters for KEITHLEY 237 for I-V Characteristics

Start Value (V)	Stop Value (V)	Steps Count	Current Limit (A)	Time Interval (ms)	Bias (v)
-100	+100	20	0.1	500	0

This way was used from the other for many materials to measure the sensitivity for humidity, gases, and vapor for many organic solvents [10,11]

The I-V characteristics for each prepared film is studied in air and in 100 ppm of methanol vapor at different temperature (50-350 °C) for three films their dimensions of particle about (216.31, 72.19, 75.2nm).

We can calculate the resistance in air and in 100 ppm of methanol vapor from the I-V characteristics for each prepared film then sensor sensitivity was defined as the resistance ratio, $R_{\text{air}}/R_{\text{gas}}$, where R_{air} and R_{gas} stand for the electrical resistances in dry air and the sample gas, respectively.[12,13]

The sensor sensitivity values $[(R_{\text{air}}/R_{\text{gas}}) \times 100]$ to 100 ppm of methanol in the temperature range from (50-350 °C) at three different milling times are shown in Figure. 5.

Figure 5. The sensitivity $S = [(R_{\text{air}}/R_{\text{gas}}) \times 100]$ to 100 ppm of methanol as a function of temperature for three films of WO_3

We note from figure 5 improving in sensitivity of three films with increasing temperature until specific temperature degree due to increasing constitute of self-defects on the surface of the film which formed from the indiscriminate expulsion of oxygen which leads to formation of oxygen gaps that gas atoms can be stabilized place then by progressing and increasing of expulsion process with high temperature to get a maximum number of defects at a specific temperature degree that called critical temperature, which the sensitivity be as high as possible, this temperature degree can be called as an operating temperature for the sensor [14]. So the temperature is an important factor in gas sensors of semiconducting metal oxides, the sensitivity is increasing and arriving up to high limits at specific temperature degree then decreasing with increasing the temperature degree this agree with scientific paper [12,15], among these three films we show that the film which has the smallest granular size 72.19nm has a high sensitivity, so we can say that the responsible of the marked advance the sensitivity toward methanol vapor is the nano structure according to scientific paper [14]

4. CONCLUSION

The thick-film devices using WO_3 nano powder prepared from the WO_3 oxide as micropowder by HEBM were promoted markedly for the sensor sensitivity to methanol vapor when milling time was set adequately (between 9 and 15 h). The promotion of the sensitivity to methanol vapor resulted from the change from micro to nano structure. After 15 h of milling the nano powder become consisting of two or more nano particle and the nano powder size increased which produced decreasing in the methanol sensitivity.

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